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# Ab Initio Study of Aziridines and Diaziridines: Nitrogen Inversion, Ring Opening, and Thermochemistry

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The chemistry of a series of aziridines and diaziridines, including the parent compounds aziridine and diaziridine and several methyl-substituted analogues, is studied by high-level ab initio methods. The electronic structure methods employed include second-order Møller−Plesset perturbation theory (MP2), the coupled cluster singles and doubles method with a perturbative correction for connected triple substitutions [CCSD(T)], and the Brueckner doubles method with analogous corrections for triple and quadruple substitutions [BD(TQ)]. Computations are carried out with basis sets ranging in size and quality from 6-31G* and cc-pVDZ to cc-pV5Z. Stationary points for nitrogen inversion are located on the ground-state potential energy surfaces, and high-level barriers to nitrogen inversion are obtained. Thermodynamic activation parameters and deuterium isotope effects are computed for nitrogen inversion and compared with experimental results. The energetics are investigated for the conrotatory ring opening of aziridine, which produces an immonium ylide. Finally, accurate values are determined for the heat of formation of aziridine and diaziridine by application of high-level focal-point thermochemical analyses.

## Introduction

Three-membered heterocycles are highly reactive molecules, in part due to ring strain. Because of their high reactivity, these small heterocycles play an important role in organic chemistry and are widely used, for example, as intermediates in organic synthesis.[1] Among three-membered heterocycles, aziridines constitute a particularly versatile class of molecules, and as discussed in several reviews,[1−4] both physical properties and chemical reactions of aziridines have been the subject of many theoretical and experimental investigations. Whereas aziridine chemistry has received much attention, relatively little work has been done on the chemistry and properties of diaziridines. The present investigation focuses on nitrogen inversion, ring opening, and thermochemistry of a series of aziridines and diaziridines, including the parent compounds aziridine and diaziridine and several methyl-substituted analogues.

Thermodynamic activation parameters for nitrogen inversion in aziridines have been obtained by NMR spectroscopy. Carter et al.[5] determined the inversion barrier in aziridine and (*N*-D)-aziridine by total band shape analysis of gas-phase $^1$H NMR spectra and obtained the thermodynamic activation parameters $\Delta G_{338}^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$. By subtracting the estimated contribution from tunneling and zero-point vibrational energy from their value for $\Delta H^{\ddagger}$ for (*N*-D)aziridine, a classical barrier height of 19.1 kcal mol$^{-1}$ was obtained. Borchardt and Bauer[6] recorded gas-phase $^1$H NMR spectra for aziridine at pressures ranging from 5 to 1100 Torr and obtained $\Delta G_{298}^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ from a complete line shape analysis of the spectra. Preliminary values were also obtained for the thermodynamic activation parameters for nitrogen inversion in 2-methylaziridine. While the rate constant for inversion of 2-methylaziridine displayed the expected falloff in the low-pressure range, the rate constant for aziridine inversion did not show any pressure dependence. These observations were rationalized in terms of slow intramolecular vibrational energy redistribution in aziridine for which the density of states at the barrier height for inversion is sparse. Two recent theoretical studies of the dynamics of molecular inversion have computed rate constants for aziridine inversion; rate constants were computed by application of an instanton approach[7] and by solution of a one- or two-dimensional problem along the reaction coordinate with application of absorbing boundary conditions,[8] and the results were in good agreement with those of Carter et al. and Borchardt and Bauer.

Ab initio studies of aziridine inversion have produced classical barrier heights in the range 12.0−22.3 kcal mol$^{-1}$ at the RHF level[9−14] for basis sets of roughly double-$\zeta$ quality both with and without polarization functions. At the RHF level, omission of polarization functions on heavy atoms typically gives barriers that are too low, e.g., 12.5 kcal mol$^{-1}$ with a 6-31G basis set.[12] Inclusion of electron correlation at the MP2 and MP3 levels with the basis sets 6-31G* and 6-31G** has been found to raise the barrier slightly.[13,14] Among the semiempirical methods applied to nitrogen inversion in aziridines, MINDO generally underestimates barrier heights; for example, the MINDO prediction for the inversion barrier in aziridine is 13.8 kcal mol$^{-1}$.[15] The CNDO/2 method makes good predictions for barriers to nitrogen inversion only when parametrized especially for this purpose, and it then predicts an inversion barrier of 21.4 kcal mol$^{-1}$ for aziridine.[16] The MNDO method generally provides the best values for barriers to nitrogen inversion in aziridines,[17] and the MNDO barrier of 19.5 kcal mol$^{-1}$ for aziridine[17] agrees well with the value obtained by Carter et al. The MNDO method, however, predicts an inversion barrier of only 12.0 kcal mol$^{-1}$ for 1-methylaziridine,[17] which deviates from our value by almost 9 kcal mol$^{-1}$ (vide infra).

Vibrational frequencies for aziridine have been obtained both experimentally and theoretically. The IR spectrum of aziridine has been recorded in the gas and liquid phases, and the fundamental vibrational frequencies have been assigned.[18,19] Many frequencies have been reassigned, however, on the basis

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of ab initio computations of harmonic vibrational frequencies, employing the RHF method with basis sets of up to 6-31G** quality,[20] the MP2 method with a basis set of double-$\zeta$ plus polarization quality and a larger A(5s3p2d) (A = C, N), H(3s1p) basis,[21] and the BLYP method in conjunction with a 6-31G** basis.[7] The IR spectrum has also been obtained for 2-methylaziridine in a combined experimental and ab initio study by Rauk et al.[22] The IR spectrum of 2-methylaziridine was recorded in the gas phase and in solution. Optimum structures of the cis and trans invertomers were then located using the RHF method with a modified 6-31G* basis set [6-31G*$^{(0.3)}$] with d-function exponents of 0.3. A 6-31G*$^{(0.3)}$ RHF harmonic force field was subsequently computed for both invertomers, and a scaling procedure was applied to refine the force fields to produce frequencies in good agreement with the experimental gas-phase fundamentals. An energy difference $E_{\mathrm{cis}} - E_{\mathrm{trans}} = 0.46$ kcal mol$^{-1}$ was obtained from 6-31G** MP2 single-point energy calculations at the RHF 6-31G*$^{(0.3)}$ optimum geometries.

Several theoretical estimates are available for the heat of formation of aziridine. Boatz and Gordon[23] determined $\Delta H_{f\ 0}^{\circ}$ (aziridine) by means of two homodesmic reactions for which 6-31G(d) MP2 reaction energies were computed employing 6-31G(d) HF geometries. The two reactions yielded somewhat differing values for $\Delta H_{f\ 0}^{\circ}$, viz., 34.2 and 36.6 kcal mol$^{-1}$, respectively. Semiempirical studies by Stewart[24] and Shaffer et al.[25] obtained values for $\Delta H_{f\ 298}^{\circ}$ of 25.1, 33.1, and 31.6 kcal mol$^{-1}$ using the MNDO, AM1, and PM3 methods, respectively, and Shaffer et al. reported a value of 29.9 kcal mol$^{-1}$ obtained by using Benson's group equivalents.[26] A recent study by Raghavachari et al.[27] determined $\Delta H_{f\ 298}^{\circ}$ employing Gaussian-2 theory. Computation of $\Delta H_{f\ 298}^{\circ}$ using the usual atomization reaction yielded a value of 30.5 kcal mol$^{-1}$, whereas application of an isodesmic bond-separation reaction produced a value of 29.8 kcal mol$^{-1}$. The best experimental value available[28] for $\Delta H_{f\ 298}^{\circ}$ (aziridine) is 30.2 ± 0.2 kcal mol$^{-1}$.

In the present investigation, optimum structures and harmonic vibrational frequencies are first computed for stationary points for nitrogen inversion on the ground-state potential energy surface for a series of aziridines and diaziridines. High-level barriers to nitrogen inversion, thermodynamic activation parameters, and deuterium isotope effects are then determined. The energetics are investigated for the thermally allowed conrotatory ring opening of aziridine, which produces an immonium ylide, and finally, heats of formation of aziridine and diaziridine are computed by means of high-level focal-point analyses.

## Computational Details

The basis sets employed in this study are the 6-31G* basis set of Pople and co-workers,[29,30] the correlation-consistent cc-pVXZ [X = D (double), T (triple), Q (quadruple), and 5 (quintuple)] basis sets of Dunning,[31] and a triple-$\zeta$ (TZ) basis with two sets of polarization functions appended to all atoms (TZ2P). The TZ2P set is a Huzinaga−Dunning[32,33] H(4s/3s), A(9s5p/5s3p) (A = C, N) basis, with exponents for H scaled by a factor[33] of 1.2$^2$, augmented with polarization functions with exponents $\alpha_p(\mathrm{H}) = (1.50, 0.375)$, $\alpha_d(\mathrm{C}) = (1.50, 0.375)$, and $\alpha_d(\mathrm{N}) = (1.60, 0.40)$. For the 6-31G* and TZ2P basis sets Cartesian d functions were used, whereas pure angular momentum d and f manifolds were employed for the correlation-consistent basis sets.

Optimum geometries were located with the restricted Hartree−Fock[34−36] (RHF) method as well as second-order Møller−Plesset perturbation theory[37,38] (MP2) using analytic gradient techniques.[39−41] Harmonic vibrational frequencies were computed at all located stationary points at the RHF and MP2 levels by means of analytic second derivative techniques.[39,42−45] Higher-order dynamical electron correlation was accounted for by the coupled cluster singles and doubles method (CCSD),[46−50] the CCSD method augmented with a perturbative contribution from connected triple excitations [CCSD(T)],[51] and the Brueckner doubles method (BD) with analogous corrections for triple and quadruple substitutions [BD(TQ)].[52,53] In the correlated calculations, the carbon and nitrogen 1s core orbitals were frozen, whereas all virtual orbitals were correlated.

The determination of heats of formation and of the inversion barrier for aziridine employs reaction energies and barriers obtained by the focal-point method of Allen and co-workers.[54−57] The focal-point method is an extrapolation scheme used to obtain accurate, converged predictions for relative energies, and it utilizes the rapid convergence of the higher-order correlation increments for the relative energies with respect to basis set augmentation. The focal-point method, as employed here, entails computation of MP2 relative energies using the cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets, extrapolation of the MP2 correlation energies to the infinite basis set limit, and addition of a cc-pVTZ MP2 → CCSD(T) correction (and, in some cases, a cc-pVDZ CCSD(T) → BD(TQ) correction). MP2 correlation energies at the infinite basis set limit [$E^{(2)}(\infty)$] were obtained by extrapolation of the MP2 correlation energies for the cc-pVDZ-QZ series by means of the formula[58]

$$E^{(2)}(l_{\max}) = E^{(2)}(\infty) + B(l_{\max} + 1)^{-4} + C(l_{\max} + 1)^{-5}$$

where $l_{\max}$ denotes the highest angular momentum represented in the basis set.

The electronic structure computations were carried out with the program packages Gaussian 94[59] and MPQC.[60−63]

## Optimum Geometric Structures and Harmonic Vibrational Frequencies

Stationary points on the reaction paths for nitrogen inversion were located at the 6-31G* MP2 level of theory for the series of aziridines and diaziridines depicted in Figure 1, and the optimum geometrical parameters are listed in Tables 1 and 2. The 6-31G* MP2 level accurately reproduces the microwave ($r_s$) structure of aziridine obtained by Bak and Skaarup[64] (Table 1), yielding bond distances within 0.005 Å and bond angles within 1° of the experimental values. The effect of basis set improvement was investigated for aziridine by performing an MP2 geometry optimization with the TZ2P basis set. The most significant structural changes accompanying basis set augmentation from 6-31G* to TZ2P at the MP2 level are elongation of the N−C bonds and shortening of the N−H and C−H bonds by ca. 0.01 Å as well as an increase in the N−H out-of-plane angle and the H−C−H angles by about 1°. While the TZ2P MP2 bond angles on average agree slightly better with experiment than do the 6-31G* MP2 angles, the 6-31G* basis more accurately reproduces bond distances, and the optimum geometries for the other aziridines and diaziridines were therefore computed at the 6-31G* MP2 level of theory.

The C−C distance in aziridine (1.480 Å at the 6-31G* MP2 level) is about 0.03 Å shorter than in cyclopropane [$r_0$(C−C) = 1.512 Å[65]]. Introduction of the more electronegative nitrogen atom into the ring increases the p-character of the orbitals on each carbon atom directed toward nitrogen; the s-character of the C−C bonding orbitals therefore increases, and the C−C

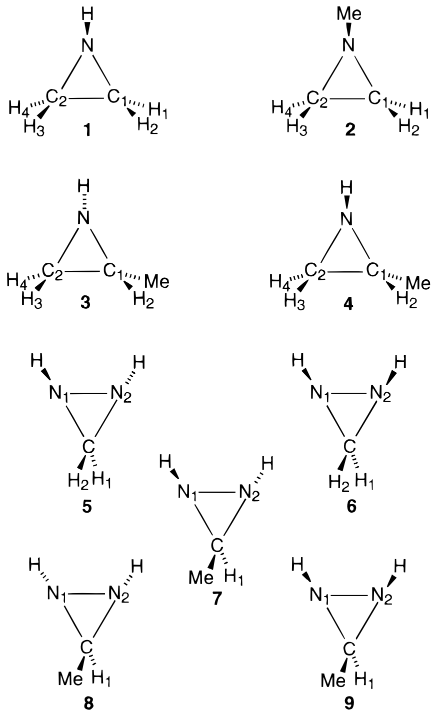

**Figure 1.** Structure and assumed numbering of atoms for aziridines and diaziridines. For all methyl-substituted compounds, the methyl group conformation is staggered. The names and point group symmetries of the depicted molecules are (**1**) aziridine ($C_s$), (**2**) 1-methylaziridine ($C_s$), (**3**) *cis*-2-methylaziridine ($C_1$), (**4**) *trans*-2-methylaziridine ($C_1$), (**5**) *trans*-diaziridine ($C_2$), (**6**) *cis*-diaziridine ($C_s$), (**7**) *r*-1,*t*-2,*c*-3-methyldiaziridine ($C_1$), (**8**) *r*-1,*c*-2,*t*-3-methyldiaziridine ($C_s$), and (**9**) *r*-1,*c*-2,*c*-3-methyldiaziridine ($C_s$).

bond shortens. Likewise, the N−C distance in diaziridine is about 0.02 Å shorter than in aziridine (1.450 vs 1.474 Å).

Comparison of the geometry of aziridine and 1-methylaziridine shows that *N*-methyl substitution significantly changes the ring geometry. Thus, upon *N*-methyl substitution, the N−C distance in the ring decreases by about 0.01 Å (from 1.474 to 1.463 Å). Also, the C−N−C angle increases from 60.3° to 61.1°, and this opening of the angle is accompanied by an increase in the C−C bond distance from 1.480 to 1.486 Å. The opening of the ring angle centered on the methyl-substituted atom and the concomitant elongation of the opposite bond are also observed for the other methyl-substituted aziridines and diaziridines.

In the transition states, the inverting nitrogen atom is $sp^2$ hybridized and has a planar (or near-planar) configuration. Compared with the minimum geometries, the $sp^2$ hybridization in the transition state gives shorter bonds to the inverting nitrogen atom and a larger value for the ring angle centered on this atom. For instance, in aziridine the N−C distance and C−N−C angle assume values of 1.474 Å and 60.3°, respectively, whereas the corresponding values in the transition state for inversion are 1.401 Å and 66.0°.

Harmonic vibrational frequencies for aziridine and 2-methylaziridine are listed in Table 3 along with the experimental fundamental frequencies. Assignments of the vibrational modes for aziridine[20,21] and 2-methylaziridine[22] have been presented elsewhere. The harmonic vibrational frequencies were computed at the MP2 level using the 6-31G* and TZ2P basis sets for aziridine and the 6-31G* set for 2-methylaziridine. The 6-31G* MP2 frequencies for aziridine are 4−7% higher than their experimental counterparts, except for mode 18, which is about 10% higher than the experimental value. On average, the 6-31G* MP2 frequencies for aziridine are 5.9% higher than the experimentally obtained fundamentals. The agreement between theory and experiment is somewhat improved at the TZ2P MP2 level, with theoretical frequencies being on average 3.7% too high and individual frequencies overshooting by 1−7%. In particular, except for the highest five frequencies which all represent C−H and N−H stretching modes, all frequencies are significantly improved by basis set augmentation. The improvement of MP2 frequencies with basis set augmentation was also noted by Simandiras et al.[21] For *trans*- and *cis*-2-methylaziridine the 6-31G* MP2 frequencies are, on average, higher than the experimental fundamentals by 5.5% and 5.9%, respectively. Individual frequencies overshoot the experimental values by ca. 5−8%, except for the three lowest modes (25−27) which all involve $CH_3$ torsion or bending. The above observations indicate that a scale factor of ca. 0.95 applied to 6-31G* MP2 harmonic vibrational frequencies should significantly improve the agreement with experimental fundamental frequencies for the aziridines and diaziridines presented in this work; however, the scale factor may not improve the ab initio values for very low-frequency modes involving $CH_3$ bending or torsion. Table 4 lists 6-31G* MP2 harmonic vibrational frequencies for diaziridines and methyl-substituted aziridines, and frequencies for the transition states for nitrogen inversion are listed in Table 5. For computation of isotope effects (vide infra) harmonic vibrational frequencies for minima and transition states for nitrogen inversion in (*N*-D)aziridine and (*N*-D)*trans*-2-methylaziridine were also computed, and these frequencies are given as Supporting Information (Table 1S).

## Nitrogen Inversion

**Barrier Height.** Classical barrier heights for nitrogen inversion were obtained by computation of single-point energies at optimum 6-31G* MP2 geometries. The barrier to nitrogen inversion in aziridine was first determined by the focal-point method. The focal-point scheme is detailed in Table 6, and total energies are given as Supporting Information (Table 2S). The focal-point method here entails determination of an extrapolated infinite basis set MP2 barrier height to which the cc-pVTZ MP2 → CCSD(T) and cc-pVDZ CCSD(T) → BD(TQ) shifts in the barrier are added. The convergence pattern with respect to basis set improvement for the higher-order (beyond MP2) correlation corrections to the barrier height lends confidence to this scheme; thus the MP2 → CCSD(T) increment appears to be essentially converged with the cc-pVTZ basis set, and the CCSD(T) → BD(TQ) correction is minuscule with the cc-pVDZ set and probably also with larger basis sets. The focal-point barrier $\Delta E_e^{\ddagger} = 18.98$ kcal mol$^{-1}$ is in excellent agreement with the barrier height of 19.1 kcal mol$^{-1}$ obtained by Carter et al.[5]

We note that the inversion barrier computed at the cc-pVQZ MP2 level of theory, $\Delta E_e^{\ddagger} = 18.9$ kcal mol$^{-1}$, is very close to the focal-point barrier because of near-cancellation of the basis set incompleteness error (≈0.4 kcal mol$^{-1}$) and the error due to incomplete treatment of electron correlation (≈0.5 kcal mol$^{-1}$). On the basis of this result, cc-pVQZ MP2 classical barrier heights were computed for the other aziridines and diaziridines to avoid the computationally somewhat expensive focal-point scheme. The barrier heights thus obtained are given in Table 7, which also lists cc-pVQZ MP2 barriers after inclusion of a zero-point vibrational energy correction computed from 6-31G* MP2 harmonic vibrational frequencies scaled by a factor of 0.95. The following discussion of inversion barriers for aziridines and diaziridines pertains to classical barrier

**TABLE 1: Selected Optimum Geometrical Parameters for Stationary Points on the Potential Energy Surfaces for Nitrogen Inversion in Aziridines[a]**

| | minima | | | | | | transition states[b] | | |
|---|---|---|---|---|---|---|---|---|---|
| | **1**<br>6-31G*<br>MP2 | **1**<br>TZ2P<br>MP2 | **1**<br>expt[c] | **2**<br>6-31G*<br>MP2 | **3**<br>6-31G*<br>MP2 | **4**<br>6-31G*<br>MP2 | **1′**<br>6-31G*<br>MP2 | **2′**<br>6-31G*<br>MP2 | **3↔4**<br>6-31G*<br>MP2 |
| $r$(N−X)[d] | 1.021 | 1.012 | 1.016 | 1.459 | 1.023 | 1.021 | 1.000 | 1.425 | 1.002 |
| $r$(N−$C_1$) | 1.474 | 1.484 | 1.475 | 1.463 | 1.474 | 1.475 | 1.401 | 1.400 | 1.403 |
| $r$(N−$C_2$) | 1.474 | 1.484 | 1.475 | 1.463 | 1.479 | 1.478 | 1.401 | 1.400 | 1.404 |
| r($C_1$−$C_2$) | 1.480 | 1.483 | 1.481 | 1.486 | 1.480 | 1.481 | 1.526 | 1.529 | 1.527 |
| $r$($C_1$−Y)[d] | 1.085 | 1.077 | 1.083 | 1.086 | 1.506 | 1.504 | 1.093 | 1.095 | 1.511 |
| $r$($C_1$−$H_2$) | 1.087 | 1.078 | 1.084 | 1.089 | 1.088 | 1.090 | 1.093 | 1.095 | 1.096 |
| $r$($C_2$−$H_3$) | 1.087 | 1.078 | 1.084 | 1.089 | 1.086 | 1.087 | 1.093 | 1.095 | 1.094 |
| $r$($C_2$−$H_4$) | 1.085 | 1.077 | 1.083 | 1.086 | 1.088 | 1.086 | 1.093 | 1.095 | 1.093 |
| $\theta$($C_1$−N−$C_2$) | 60.3 | 59.9 | 60.3 | 61.1 | 60.2 | 60.2 | 66.0 | 66.2 | 65.9 |
| $\theta$(Y−$C_1$−N)[d] | 114.5 | 114.2 | 114.3 | 115.6 | 120.3 | 115.8 | 119.3 | 119.5 | 120.4 |
| $\theta$(Y−$C_1$−$C_2$)[d] | 119.9 | 119.3 | 119.3 | 120.5 | 120.4 | 121.8 | 117.9 | 117.9 | 120.4 |
| $\theta$($H_2$−$C_1$−N) | 118.9 | 118.2 | 118.3 | 117.8 | 112.3 | 116.8 | 119.3 | 119.5 | 117.3 |
| $\theta$($H_2$−$C_1$−$C_2$) | 118.0 | 117.7 | 117.8 | 117.2 | 117.4 | 115.8 | 117.9 | 117.9 | 115.8 |
| $\theta$($H_3$−$C_2$−N) | 118.9 | 118.2 | 118.3 | 117.8 | 114.7 | 119.0 | 119.3 | 119.4 | 119.3 |
| $\theta$($H_3$−$C_2$−$C_1$) | 118.0 | 117.7 | 117.8 | 117.2 | 120.5 | 118.6 | 117.9 | 118.0 | 117.3 |
| $\theta$($H_4$−$C_2$−N) | 114.5 | 114.2 | 114.3 | 115.6 | 118.7 | 114.4 | 119.3 | 119.4 | 119.3 |
| $\theta$($H_4$−$C_2$−$C_1$) | 119.9 | 119.3 | 119.3 | 120.5 | 117.5 | 119.5 | 117.9 | 118.0 | 118.5 |
| $\theta$(Y−$C_1$−$H_2$)[d] | 114.7 | 115.8 | 115.7 | 115.0 | 115.0 | 115.3 | 113.9 | 113.7 | 114.2 |
| $\theta$($H_3$−$C_2$−$H_4$) | 114.7 | 115.8 | 115.7 | 115.0 | 114.7 | 114.7 | 113.9 | 113.7 | 113.4 |
| $\gamma$[e] | 67.4 | 68.8 | 67.5 | 61.1 | 67.9 | 67.2 | 0.0 | 0.0 | 0.9[f] |

[a] Bond distances in angstroms, bond angles in degrees. Numbering of atoms and point group symmety for the minima are given in Figure 1; the transition states **1′**, **2′**, and **3↔**4 belong to the point groups $C_{2v}$, $C_s$, and $C_1$, respectively. [b] Prime superscript denotes a transition state for inversion of a structure identical to its invertomer. [c] Reference 64. [d] **1**: X = H, Y = $H_1$. **2**: X = Me, Y = $H_1$. **3** and **4**: X = H, Y = Me. [e] Angle between N−X bond and ring plane. [f] The N−H bond and the methyl group are cis.

**TABLE 2: Selected 6-31G* MP2 Optimum Geometrical Parameters for Stationary Points on the Potential Energy Surfaces for Nitrogen Inversion in Diaziridines[a]**

| | minima | | | | | transition states | | |
|---|---|---|---|---|---|---|---|---|
| | **5** | **6** | **7** | **8** | **9** | **5↔6** | **7↔8** | **7↔9** |
| $r$($N_1$−$N_2$) | 1.508 | 1.510 | 1.514 | 1.516 | 1.518 | 1.442 | 1.446 | 1.447 |
| $r$($N_1$−C) | 1.450 | 1.452 | 1.450 | 1.453 | 1.451 | 1.511 | 1.375 | 1.509 |
| $r$($N_2$−C) | 1.450 | 1.452 | 1.451 | 1.453 | 1.451 | 1.372 | 1.511 | 1.376 |
| r($N_1$−H) | 1.023 | 1.026 | 1.025 | 1.027 | 1.028 | 1.034 | 1.000 | 1.034 |
| $r$($N_2$−H) | 1.023 | 1.026 | 1.024 | 1.027 | 1.028 | 0.999 | 1.035 | 1.000 |
| $r$(C−$H_1$) | 1.087 | 1.085 | 1.090 | 1.092 | 1.088 | 1.091 | 1.098 | 1.094 |
| $r$(C−X)[b] | 1.087 | 1.089 | 1.501 | 1.498 | 1.503 | 1.095 | 1.503 | 1.508 |
| $\theta$($N_1$−C−$N_2$) | 62.7 | 62.6 | 62.9 | 62.9 | 63.1 | 59.8 | 59.9 | 60.0 |
| $\theta$(H−$N_1$−C) | 108.4 | 107.7 | 108.0 | 108.1 | 107.2 | 104.7 | 158.2 | 104.4 |
| $\theta$(H−$N_2$−C) | 108.4 | 107.7 | 108.9 | 108.1 | 107.2 | 157.3 | 105.1 | 158.0 |
| $\theta$($H_1$−C−$N_1$) | 114.7 | 115.5 | 112.6 | 117.1 | 113.2 | 114.6 | 117.8 | 112.3 |
| $\theta$($H_1$−C−$N_2$) | 119.9 | 115.5 | 117.9 | 117.1 | 113.2 | 119.9 | 115.0 | 117.9 |
| $\theta$(X−C−$N_1$)[b] | 119.9 | 119.1 | 121.5 | 116.7 | 121.0 | 116.8 | 121.1 | 119.7 |
| $\theta$(X−C−$N_2$)[b] | 114.7 | 119.1 | 116.3 | 116.7 | 121.0 | 120.0 | 116.4 | 121.1 |
| $\theta$($H_1$−C−X)[b] | 115.1 | 115.1 | 115.5 | 115.9 | 115.3 | 114.4 | 114.9 | 114.6 |
| $\gamma_1$[c] | 71.1 | 69.4 | 71.5 | 69.3 | 70.0 | 61.4 | 1.2[d] | 72.4 |
| $\gamma_2$[c] | 71.1 | 69.4 | 70.7 | 69.3 | 70.0 | 9.0[d] | 72.0 | 2.9[d] |

[a] Bond distances in angstroms, bond angles in degrees. Numbering of atoms and point group symmetry for the minima are given in Figure 1; the transition states all belong to the point group $C_1$. [b] **5** and **6**: X = $H_2$. **7**−**9**: X = Me. [c] $\gamma_i$ denotes the angle between the $N_i$−H bond and the ring plane. [d] The bonds $N_1$−H and $N_2$−H are cis.

**TABLE 3: Harmonic Vibrational Frequencies and Gas-Phase Experimental Fundamental Frequencies (cm$^{-1}$) for Aziridine (1), *trans*-2-Methylaziridine (4), and *cis*-2-Methylaziridine (3)**

| | **1** ($C_s$) | | | **4** ($C_1$) | | **3** ($C_1$) | |
|---|---|---|---|---|---|---|---|
| mode | 6-31G*<br>MP2 | TZ2P<br>MP2 | expt[a] | 6-31G*<br>MP2 | expt[b] | 6-31G*<br>MP2 | expt[b] |
| 1 | a′ 3528 | 3558 | 3338 | a 3519 | 3343 | a 3501 | 3320 |
| 2 | 3294 | 3294 | 3079 | 3279 | 3065 | 3281 | 3066 |
| 3 | 3196 | 3187 | 3015 | 3208 | 2981 | 3211 | 3007 |
| 4 | 1587 | 1545 | 1482 | 3191 | *c* | 3188 | *c* |
| 5 | 1340 | 1312 | 1268 | 3187 | *c* | 3184 | *c* |
| 6 | 1284 | 1232 | 1211 | 3182 | 2939 | 3180 | *c* |
| 7 | 1156 | 1119 | 1090 | 3105 | 2882 | 3095 | 2878 |
| 8 | 1043 | 1023 | 998 | 1575 | 1496 | 1574 | 1481 |
| 9 | 912 | 868 | 856 | 1560 | 1457 | 1565 | 1475 |
| 10 | 802 | 791 | 773 | 1549 | 1444 | 1549 | 1464 |
| 11 | a″ 3283 | 3282 | 3079 | 1504 | 1412 | 1485 | 1400 |
| 12 | 3190 | 3181 | 3003 | 1456 | 1371 | 1457 | 1373 |
| 13 | 1554 | 1517 | 1463 | 1321 | 1250 | 1342 | 1268 |
| 14 | 1307 | 1274 | 1237 | 1307 | 1243 | 1297 | 1237 |
| 15 | 1192 | 1173 | 1131 | 1279 | 1210 | 1279 | 1218 |
| 16 | 1137 | 1119 | 1095 | 1191 | 1137 | 1207 | 1146 |
| 17 | 942 | 918 | 904 | 1149 | 1096 | 1180 | 1114 |
| 18 | 900 | 830 | 817 | 1128 | 1069 | 1133 | 1080 |
| 19 | | | | 1056 | 1005 | 1056 | 1007 |
| 20 | | | | 1021 | 961 | 1005 | 949 |
| 21 | | | | 972 | 929 | 970 | 926 |
| 22 | | | | 915 | 871 | 934 | 891 |
| 23 | | | | 863 | 818 | 866 | 818 |
| 24 | | | | 808 | 764 | 801 | 756 |
| 25 | | | | 405 | 401 | 409 | 401 |
| 26 | | | | 364 | 387 | 366 | *c* |
| 27 | | | | 219 | 200 | 238 | 213 |

[a] Reference 19. [b] Reference 22. [c] Not assigned.

heights; inclusion of a zero-point vibrational energy correction lowers the inversion barriers by 0.9−2.6 kcal mol$^{-1}$ but does not change any qualitative statements made below.

Comparison of inversion barriers for aziridine and 1-methylaziridine shows the barrier to increase by 1.8 kcal mol$^{-1}$ (from 18.9 to 20.7 kcal mol$^{-1}$) upon methyl substitution on N. This finding is in accordance with the general observation that nonbulky alkyl substituents on N increase the inversion barrier in aziridines.[3] Methyl substitution on a carbon atom in aziridine produces 2-methylaziridine, for which the two invertomers, *cis*- and *trans*-2-methylaziridine, are diastereomers and not isoenergetic. The barriers for inversion of the cis- and trans-isomers are therefore different, although both are close to the inversion barrier in aziridine as methyl substitution on a carbon atom leaves the electronic environment of the nitrogen atom largely unaffected. The computed energy difference $E_{\text{cis}} - E_{\text{trans}}$ is 0.5

**TABLE 4: 6-31G* MP2 Harmonic Vibrational Frequencies ($cm^{-1}$) for Aziridines and Diaziridines**

| **2** ($C_s$) | **5** ($C_2$) | **6** ($C_s$) | **7** ($C_1$) | **8** ($C_s$) | **9** ($C_s$) |
|---:|---:|---:|---:|---:|---:|
| a′ 3279 | a 3491 | a′ 3461 | a 3487 | a′ 3454 | a′ 3436 |
| 3174 | 3184 | 3289 | 3470 | 3227 | 3220 |
| 3156 | 1589 | 3178 | 3208 | 3166 | 3178 |
| 3035 | 1439 | 1587 | 3197 | 3113 | 3092 |
| 1580 | 1275 | 1379 | 3188 | 1553 | 1563 |
| 1556 | 1242 | 1264 | 3106 | 1530 | 1489 |
| 1498 | 993 | 1211 | 1559 | 1455 | 1461 |
| 1361 | 781 | 998 | 1547 | 1334 | 1375 |
| 1257 | b 3499 | 757 | 1515 | 1295 | 1293 |
| 1167 | 3280 | a″ 3434 | 1458 | 1194 | 1196 |
| 1135 | 1368 | 1410 | 1420 | 1031 | 1031 |
| 1062 | 1228 | 1221 | 1341 | 950 | 943 |
| 856 | 1174 | 1181 | 1296 | 733 | 714 |
| 778 | 1003 | 970 | 1250 | 425 | 444 |
| 395 | 915 | 870 | 1205 | a″ 3427 | a″ 3412 |
| a″ 3268 |  |  | 1164 | 3200 | 3194 |
| 3203 |  |  | 1038 | 1548 | 1543 |
| 3169 |  |  | 1031 | 1402 | 1394 |
| 1558 |  |  | 952 | 1207 | 1250 |
| 1542 |  |  | 889 | 1131 | 1182 |
| 1233 |  |  | 743 | 1008 | 1002 |
| 1188 |  |  | 437 | 862 | 879 |
| 1134 |  |  | 385 | 385 | 382 |
| 1047 |  |  | 230 | 217 | 254 |
| 907 |  |  |  |  |  |
| 393 |  |  |  |  |  |
| 252 |  |  |  |  |  |

**TABLE 5: 6-31G* MP2 Harmonic Vibrational Frequencies ($cm^{-1}$) for Transition States for Nitrogen Inversion in Aziridines and Diaziridines**

| **1′** ($C_{2v}$) | **2′** ($C_s$) | **3↔4** ($C_1$) | **5↔6** ($C_1$) | **7↔8** ($C_1$) | **7↔9** ($C_1$) |
|---:|---:|---:|---:|---:|---:|
| $a_1$ 3808 | a′ 3188 | a 3791 | a 3841 | a 3827 | *a* 3829 |
| 3121 | 3098 | 3200 | 3319 | 3312 | 3318 |
| 1623 | 3091 | 3185 | 3209 | 3226 | 3200 |
| 1384 | 3049 | 3183 | 3112 | 3192 | 3189 |
| 1163 | 1661 | 3111 | 1611 | 3108 | 3145 |
| 892 | 1586 | 3108 | 1423 | 3094 | 3100 |
| $a_2$ 3186 | 1573 | 3098 | 1407 | 1562 | 1565 |
| 1186 | 1553 | 1605 | 1277 | 1544 | 1541 |
| 1071 | 1504 | 1564 | 1208 | 1530 | 1517 |
| $b_1$ 3198 | 1268 | 1547 | 1132 | 1455 | 1458 |
| 1214 | 1163 | 1496 | 1070 | 1413 | 1413 |
| 887 | 1161 | 1455 | 982 | 1384 | 1381 |
| 980i | 1059 | 1360 | 943 | 1257 | 1261 |
| $b_2$ 3114 | 1039 | 1219 | 804 | 1198 | 1223 |
| 1576 | 724 | 1199 | 1196i | 1104 | 1108 |
| 1188 | 331 | 1188 |  | 1056 | 1068 |
| 1163 | a″ 3171 | 1175 |  | 1031 | 1025 |
| 1002 | 3159 | 1160 |  | 999 | 998 |
|  | 3103 | 1064 |  | 894 | 892 |
|  | 1537 | 1028 |  | 761 | 755 |
|  | 1205 | 951 |  | 449 | 450 |
|  | 1184 | 921 |  | 379 | 387 |
|  | 1154 | 814 |  | 230 | 251 |
|  | 1053 | 430 |  | 1182i | 1188i |
|  | 864 | 370 |  |  |  |
|  | 59 | 235 |  |  |  |
|  | 404i | 969i |  |  |  |

**TABLE 6: Evaluation of Barrier Height for Nitrogen Inversion in Aziridine[a]**

|  | cc-pVDZ | cc-pVTZ | cc-pVQZ | ∞ |
|---|---|---|---|---|
| $\Delta E_e^\ddagger$[RHF] | 19.46 | 18.49 | 18.18 | [18.05][b] |
| $\delta$[MP2] | +1.31 | +1.00 | +0.73 | +0.42[c] |
| $\delta$[CCSD] | +0.11 | +0.11 | [+0.11] | [+0.11] |
| $\delta$[CCSD(T)] | +0.38 | +0.36 | [+0.36] | [+0.36] |
| $\delta$[BD(TQ)] | +0.04 | [+0.04] | [+0.04] | [+0.04] |
| $\Delta E_e^\ddagger$(corr) | 21.30 | [20.01] | [19.42] | [18.98] |
| $\Delta E_e^\ddagger$(focal-point) = 18.98 kcal mol$^{-1}$ |  |  |  |  |

[a] All entries in kcal mol$^{-1}$. Increments in brackets are assumed values. The symbol $\delta$ denotes the increment in the barrier ($\Delta E_e^\ddagger$) relative to the preceding level of theory. [b] cc-pV5Z RHF value. [c] Extrapolated to the infinite basis set limit (see text).

**TABLE 7: cc-pVQZ MP2 Energetics for Nitrogen Inversion in Aziridines and Diaziridines[a]**

| species | $E_{\mathrm{total}}$ | $E_{\mathrm{ZPVE}}$[b] | $\Delta E_e^\ddagger$ | $\Delta E_0^\ddagger$ |
|---|---|---|---|---|
| aziridine | −133.686 339 | 42.98 | 18.91 | 17.72 |
| 1-methylaziridine | −172.914 709 | 60.00 | 20.71 | 19.84 |
| *trans*-2-methylaziridine | −172.927 535 | 60.19 | 19.08 | 17.90 |
| *cis*-2-methylaziridine | −172.926 714 | 60.23 | 18.57 | 17.35 |
| *trans*-diaziridine[c] | −149.702 062 | 35.93 | 31.10 | 29.58 |
| *trans*-diaziridine[d] |  |  | 69.05 | 66.47 |
| *cis*-diaziridine[c] | −149.693 925 | 35.60 | 25.99 | 24.80 |
| *cis*-diaziridine[d] |  |  | 63.94 | 61.69 |
| 3-methyldiaziridine (**7**)[e] | −188.945 645 | 53.12 | 30.43 | 28.92 |
| 3-methyldiaziridine (**7**)[f] |  |  | 31.16 | 29.75 |
| 3-methyldiaziridine (**8**)[e] | −188.938 477 | 52.76 | 25.93 | 24.78 |
| 3-methyldiaziridine (**9**)[f] | −188.936 806 | 52.87 | 25.61 | 24.45 |

[a] Total energies ($E_{\mathrm{total}}$) in hartrees; zero-point vibrational energies ($E_{\mathrm{ZPVE}}$), classical barrier heights for inversion ($\Delta E_e^\ddagger$), and ZPVE corrected barrier heights ($\Delta E_0^\ddagger$) in kcal mol$^{-1}$. [b] Computed from 6-31G* MP2 harmonic vibrational frequencies scaled by 0.95. [c] Inversion on one nitrogen atom interconverting *cis*- and *trans*-diaziridine. [d] Synchronous inversion on both nitrogen atoms via biplanar second-order saddle point. [e] Inversion on one nitrogen atom interconverting **7** and **8**. [f] Inversion on one nitrogen atom interconverting **7** and **9**.

kcal mol$^{-1}$, and the inversion barriers for the cis- and trans-isomers are 18.6 and 19.1 kcal mol$^{-1}$, respectively.

In diaziridine a single inversion on either one of the nitrogen atoms also interconverts two diastereomers, *cis*- and *trans*-diaziridine. The barrier for inversion of the trans-isomer is 31.1 kcal mol$^{-1}$, and for inversion of *cis*-diaziridine the barrier is 26.0 kcal mol$^{-1}$. The rather large energy difference of 5.1 kcal mol$^{-1}$ between the trans- and cis-isomers may be ascribed to repulsion between the two cis lone pairs on adjacent nitrogen atoms in *cis*-diaziridine. Nitrogen inversion in diaziridine may conceivably occur synchronously on both nitrogen atoms, proceeding via a "biplanar" stationary point with both nitrogen atoms $sp^2$ hybridized. We have found this structure to be a second-order saddle point (at the 6-31G* MP2 level of theory), and cc-pVQZ MP2 single-point energy calculations predict it to lie 63.9 kcal mol$^{-1}$ above *cis*-diaziridine.

Substitution of a methyl group on the carbon atom in diaziridine yields 3-methyldiaziridine, for which there are three energetically different diastereomers, structures **7**−**9**, that can be interconverted by nitrogen inversion. Starting from **7**, the most stable isomer, inversion on $N_1$ (see Figure 1) produces **8** via a barrier of 30.4 kcal mol$^{-1}$, whereas inversion on $N_2$ proceeds with a barrier of 31.2 kcal mol$^{-1}$ and yields structure **9**. For the reverse processes (**8** → **7** and **9** → **7**), the barriers are 25.9 and 25.6 kcal mol$^{-1}$, respectively.

The computed inversion barriers for diaziridines and aziridines agree with the general trend that barriers to nitrogen inversion in diaziridines are higher than in aziridines. This trend may be explained by electronegativity arguments in analogy with the situation for N-substituted aziridines, where the barrier (for nonbulky substituents) is known to increase with increasing electronegativity of the substituent on N.[3]

**Thermodynamic Activation Parameters and Isotope Effects.** For the aziridines included in this study, experimental values are available for the thermodynamic activation parameters $\Delta H^\ddagger$, $\Delta S^\ddagger$, and $\Delta G^\ddagger$ for nitrogen inversion. The experimental results are summarized in Table 8 together with ab initio values computed in this work. The ab initio values were obtained by applying zero-point vibrational energy and temperature correc-

**TABLE 8: Thermodynamic Activation Parameters for Nitrogen Inversion in Aziridines[a]**

| | $T$ (K) | $\Delta H^\ddagger$ (kcal mol$^{-1}$) | $\Delta S^\ddagger$ (eu) | $\Delta G^\ddagger$ (kcal mol$^{-1}$) |
|---|---|---|---|---|
| | | Aziridine | | |
| expt[b] | 338 | 15.2 ± 0.4 | −6.2 ± 1.4 | 17.23 ± 0.05 |
| theory[d,e] | 338 | 17.63 | −1.76 | 18.23 |
| theory[d,f] | 338 | 15.93 | −5.25 | 17.71 |
| expt[c] | 298 | 15.2 ± 0.4 | −5.5 ± 3 | 16.8 ± 0.5 |
| theory[d,e] | 298 | 17.67 | −1.66 | 18.17 |
| theory[d,f] | 298 | 16.00 | −5.15 | 17.54 |
| | | (*N*-D)Aziridine | | |
| expt[b] | 338 | 17.3 ± 0.6 | −1.4 ± 2.0 | 17.80 ± 0.05 |
| theory[d,e] | 338 | 17.92 | −1.85 | 18.54 |
| theory[d,f] | 338 | 17.12 | −3.35 | 18.25 |
| | | 1-Methylaziridine | | |
| expt[g] | 390 | | | 19.03 |
| theory[d,e] | 390 | 19.71 | 1.69 | 19.05 |
| | | 2-Methylaziridine (trans to cis) | | |
| expt[c] | 298 | 18.4 | 4 | 17.0 |
| theory[d,e] | 298 | 17.83 | −0.43 | 17.96 |
| theory[d,f] | 298 | 16.21 | −3.79 | 17.35 |
| | | (*N*-D)2-Methylaziridine (trans to cis) | | |
| theory[d,e] | 298 | 18.13 | −0.49 | 18.27 |
| theory[d,f] | 298 | 17.38 | −1.91 | 17.94 |

[a] All reported experimental values were obtained in the gas phase. [b] Reference 5. [c] Reference 6. [d] Obtained by applying zero-point vibrational energy and thermochemical corrections to the cc-pVQZ MP2 classical barrier height (see text). [e] Tunneling not included. [f] Tunneling included (see text). [g] Reference 68.

tions to the cc-pVQZ MP2 classical barrier heights. These corrections were computed using 6-31G* MP2 harmonic vibrational frequencies scaled by a factor of 0.95 and standard formulas from statistical mechanics.[66] For aziridine inversion, Carter et al.[5] found that model calculations of the isotope effect, employing an experimental geometry and an estimated diagonal force field, could reproduce the experimental results only if tunneling was taken into account. Application of a simple tunneling correction, computed from Bell's equation (vide infra), was found to bring the calculated values into good agreement with experiment. On the basis of this result, we have applied the same tunneling correction obtained from Bell's equation for tunneling through a parabolic barrier[67]

$$Q_{\mathrm{t}} = \frac{{}^{1}/_{2}u_{\mathrm{t}}}{\sin({}^{1}/_{2}u_{\mathrm{t}})}$$

$$u_{\mathrm{t}} = \frac{h|\nu|}{kT}$$

where $Q_{\mathrm{t}}$ represents the tunneling correction to the reaction rate, and $\nu$ is the reaction coordinate frequency in the transition state. The tunneling correction to $\Delta G^\ddagger$ is expressed as

$$\Delta G_{\mathrm{tunnel}} = -RT \ln Q_{\mathrm{t}}$$

and by plotting $\Delta G_{\mathrm{tunnel}}$ (computed at several temperatures between 288 and 308 K) as a function of $T$, $\Delta H_{\mathrm{tunnel}}$ and $\Delta S_{\mathrm{tunnel}}$ can be determined.

Considering first the results for aziridine inversion at 338 K, the ab initio values without a tunneling correction for $\Delta H^\ddagger$, $\Delta S^\ddagger$, and $\Delta G^\ddagger$ are higher than their experimental counterparts by 2.4 kcal mol$^{-1}$, 4.4 eu, and 1.0 kcal mol$^{-1}$, respectively; however, for the (*N*-D) isotopomer the corresponding deviations are only 0.6 kcal mol$^{-1}$, −0.4 eu, and 0.7 kcal mol$^{-1}$. The much better agreement between the experimental and theoretical values for the (*N*-D) isotopomer is, in large part, due to tunneling, which is more important in the parent molecule. The only slightly better agreement with experiment for the $\Delta G^\ddagger$ value for the (*N*-D) isotopomer compared with the parent molecule is a consequence of partial cancellation of the errors in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the latter. Inclusion of the tunneling correction markedly improves the agreement with experiment for both isotopomers, although deviations between experiment and theory for the parent molecule are still as large as 0.7 kcal mol$^{-1}$, 1.0 eu, and 0.5 kcal mol$^{-1}$ for $\Delta H^\ddagger$, $\Delta S^\ddagger$, and $\Delta G^\ddagger$, respectively. For the isotope effects, however, inclusion of the tunneling correction brings the theoretical results into excellent agreement with experiment. The theoretical and experimental values of [$\Delta\Delta H^\ddagger$ ($=\Delta H_{\mathrm{D}}{}^\ddagger - \Delta H_{\mathrm{H}}{}^\ddagger$), $\Delta\Delta S^\ddagger$, $\Delta\Delta G^\ddagger$] are [1.19 kcal mol$^{-1}$, 1.90 eu, 0.54 kcal mol$^{-1}$] and [2.1 ± 1.2 kcal mol$^{-1}$, 4.8 ± 3.6 eu, 0.57 ± 0.07 kcal mol$^{-1}$],[5] respectively, and the theoretical values are thus well within the experimental error bars.

Experimental values for the thermodynamic activation parameters have also been obtained for the methyl-substituted aziridines 1-methylaziridine and *trans*-2-methylaziridine. For inversion of 1-methylaziridine, the experimental value of 19.03 kcal mol$^{-1}$ for $\Delta G^\ddagger$ determined at 390 K[68] agrees very well with our ab initio value of 19.05 kcal mol$^{-1}$. For *trans*-2-methylaziridine preliminary experimental values have been presented[6] at 298 K for $\Delta G^\ddagger$, $\Delta H^\ddagger$, and $\Delta S^\ddagger$, but these values are in poor agreement with our ab initio values both before and after inclusion of tunneling. Thus, without the tunneling correction the ab initio values for $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are lower than their experimental counterparts by 0.6 kcal mol$^{-1}$ and 4.4 eu, respectively, and inclusion of tunneling increases these discrepancies to 2.2 kcal mol$^{-1}$ and 7.8 eu. On the basis of the agreement between our ab initio results and experiment for aziridine, these discrepancies warrant further investigation. Although the ab initio temperature correction to $\Delta S^\ddagger$ for 2-methylaziridine contains some error due to treatment of the hindered internal rotation of the methyl group as a vibration, our value for $\Delta H^\ddagger$ does not seem compatible with the experimental result. In Table 8 we also present results for (*N*-D)2-methylaziridine, although no experimental data are available for comparison.

## Ring Opening of Aziridine

The reactions of aziridine often involve opening of the ring, either by C−N or C−C bond cleavage. The aziridine ring may also be opened in a unimolecular isomerization, and we consider such ring openings in the following. Aziridine isomerizations breaking one of the C−N bonds may lead to formation of ethyleneamine, ethanimine, or *N*-methylmethanimine. These ring openings all require a (1,2)-hydrogen shift to form a stable product, and our preliminary 6-31G* MP2 calculations suggest that they are associated with barriers greater than 70 kcal mol$^{-1}$. We consider in detail here only the unimolecular ring opening that breaks the C−C bond and has a somewhat smaller barrier. The conrotatory ring opening is thermally allowed and is of interest for nitrogen inversion, because the formed immonium ylide intermediate may recyclize to form the inverted form of the aziridine molecule.

Figure 2 depicts optimum 6-31G* MP2 structures for the transition state for conrotatory ring opening of aziridine and for the formed immonium ylide and also lists cc-pVQZ MP2 energies and scaled 6-31G* MP2 zero-point vibrational energies. The immonium ylide has $C_2$ symmetry; it is nearly planar and is very close to $C_{2v}$ symmetry. The planar $C_{2v}$ structure is a transition state via which the immonium ylide may "invert";

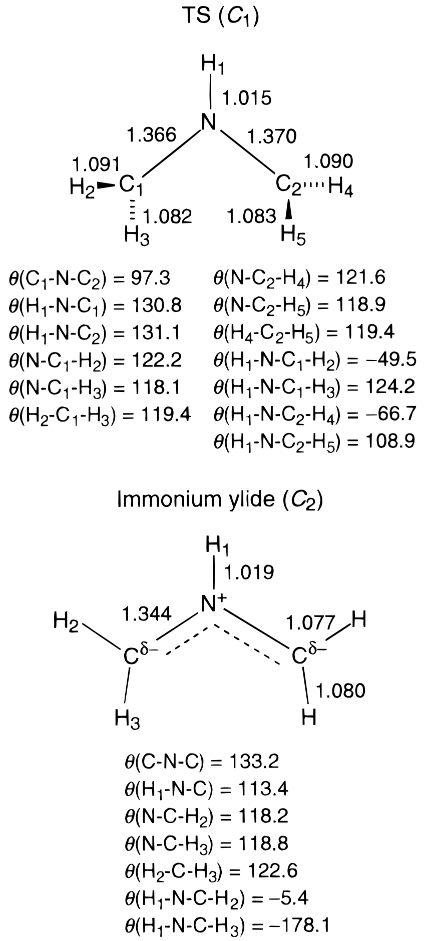

**Figure 2.** Optimum 6-31G* MP2 structures for the transition state for conrotatory ring opening of aziridine and for the immonium ylide. Bond distances are given in angstroms, bond angles in degrees. The cc-pVQZ MP2 total energies for the transition state and the immonium ylide, computed at 6-31G* MP2 optimum geometries, are −133.606 888 and −133.651 285 hartrees, respectively; zero-point vibrational energies computed from 6-31G* MP2 harmonic vibrational frequencies scaled by 0.95 are 39.66 and 40.38 kcal mol$^{-1}$, respectively.

the $C_{2v}$ transition state lies only 0.003 kcal mol$^{-1}$ above the $C_2$ minimum at the 6-31G* MP2 level, and a higher level of theory would be required to establish which of these structures is the actual minimum. The transition state for the conrotatory ring opening has $C_1$ symmetry with a near-planar configuration on the nitrogen atom and is only slightly distorted from $C_2$ symmetry. At the cc-pVQZ MP2 level, the immonium ylide lies 22.0 kcal mol$^{-1}$ above aziridine, and the classical barrier height for conrotatory ring opening is 49.9 kcal mol$^{-1}$. Including a zero-point vibrational energy correction, the endothermicity and barrier are 19.4 and 46.5 kcal mol$^{-1}$, respectively. The geometric parameters for the transition state for ring opening are not all consistent with a late transition state that would be expected for an endothermic reaction. Thus, while the configuration on the nitrogen atom is nearly planar in the transition state, and the C−N bond distances of 1.37 Å are much closer to their value in the immonium ylide (1.34 Å) than in aziridine (1.47 Å), the C−N−C angle assumes a value of 97°, which is about halfway between its values in aziridine and the immonium ylide (60° and 133°, respectively).

## Heat of Formation of Aziridine and Diaziridine

Heats of formation of aziridine and *trans*-diaziridine were computed at 298.15 K by means of the reactions

$$\text{aziridine} + NH_3 + 2CH_4 \rightarrow 2CH_3NH_2 + C_2H_6 \qquad (A)$$

$$\text{aziridine} + 3C_2H_6 \rightarrow CH_3NHCH_3 + 2C_3H_8 \qquad (B)$$

$$trans\text{-diaziridine} + 2NH_3 + CH_4 \rightarrow 2CH_3NH_2 + N_2H_4 \qquad (C)$$

$$trans\text{-diaziridine} + N_2H_4 + 2C_2H_6 \rightarrow 2CH_3NHNH_2 + C_3H_8 \qquad (D)$$

for which reaction energies were computed by the focal-point method and used in conjunction with thermochemical data available in the literature or generated from ab initio calculations in the present work. Reactions A−D were selected on the basis of the availability of established thermochemical data for the species involved other than aziridine and diaziridine and the rapid convergence of the reaction energy with respect to methodological improvement. Thus, reaction A and C are isodesmic (bond-separation) reactions, and reactions B and D are homodesmotic reactions.[69] Single-point energies used in the focal-point analyses were computed at 6-31G* MP2 optimum geometries for all species in reactions A−D, and both single-point energies and optimum geometries are given as Supporting Information (Tables 3S and 4S).

$\Delta H_f°_{298.15}$ (aziridine) was computed by means of the reaction energies $\Delta E_0$ for reactions A and B determined by the focal-point method (Table 9), $\Delta H_f°_{298.15}$ values from the literature, and enthalpy differences ($H°_{298.15}-H°_0$) (Table 10). Using reaction A, $\Delta H_f°_{298.15}$ (aziridine) is computed as follows:

$$\Delta H°_{(A),298.15} = \Delta E_{0,(A)} + 2[H°_{298.15}(CH_3NH_2) - H°_0(CH_3NH_2)] + [H°_{298.15}(C_2H_6) - H°_0(C_2H_6)] - [H°_{298.15}(\text{aziridine}) - H°_0(\text{aziridine})] - [H°_{298.15}(NH_3) - H°_0(NH_3)] - 2[H°_{298.15}(CH_4) - H°_0(CH_4)] = -14.78\ \text{kcal mol}^{-1}$$

$$\Delta H_f°_{298.15}(\text{aziridine}) = 2\Delta H_f°_{298.15}(CH_3NH_2) + \Delta H_f°_{298.15}(C_2H_6) - \Delta H_f°_{298.15}(NH_3) - 2\Delta H_f°_{298.15}(CH_4) - \Delta H°_{(A),298.15} = 30.31\ \text{kcal mol}^{-1}$$

An analogous computation for reaction B yields $\Delta H°_{(B),298.15} = -24.75$ kcal mol$^{-1}$ and $\Delta H_f°_{298.15}$(aziridine) = 30.35 kcal mol$^{-1}$. Evaluation of $\Delta H_f°_{298.15}$(*trans*-diaziridine) proceeds by a similar procedure, using $\Delta E_0$ for reactions C and D (Table 9) and thermochemical data from Table 10. The computed reaction enthalpies for reactions C and D are $\Delta H°_{(C),298.15} = -4.16$ and $\Delta H°_{(D),298.15} = -18.40$ kcal mol$^{-1}$, yielding values of 55.70 and 55.85 kcal mol$^{-1}$, respectively, for $\Delta H_f°_{298.15}$(*trans*-diaziridine).

The two predictions for $\Delta H_f°_{298.15}$(aziridine) are in close agreement, and we propose a final value of 30.3 kcal mol$^{-1}$, which agrees very well with the experimental value[28] of 30.2 ± 0.2 kcal mol$^{-1}$. We note that Boatz and Gordon[23] computed $\Delta H_f°_0$(aziridine) based on reaction energies for two homodesmotic reactions of which one is identical to our reaction B. For this reaction they obtained a reaction energy $\Delta E_e = -26.3$ kcal mol$^{-1}$ by computing 6-31G(d) MP2 single point energies at 6-31G(d) HF optimum geometries. Our focal-point value for $\Delta E_e$ for this reaction is −27.04 kcal mol$^{-1}$, and a better value for $\Delta H_f°_0$(aziridine) might be obtained by correcting the result of Boatz and Gordon for this difference in reaction energies.

Considering the predictions for $\Delta H_f°_{298.15}$(*trans*-diaziridine), we note that the correlation increments to $\Delta E_e$ are somewhat

**TABLE 9: Focal-Point Evaluation of Reaction Energies Used in the Determination of the Heat of Formation of Aziridine and Diaziridine[a,b]**

| | cc-pVDZ | cc-pVTZ | cc-pVQZ | ∞ |
|---|---|---|---|---|
| Reaction A: aziridine + $NH_3$ + $2CH_4$ → $2CH_3NH_2$ + $C_2H_6$ | | | | |
| $\Delta E_e$[RHF] | −21.76 | −19.94 | −19.91 | [−19.91] |
| $\delta$[MP2] | +2.84 | +2.81 | +2.65 | +2.43[c] |
| $\delta$[CCSD] | −1.40 | −1.78 | [−1.78] | [−1.78] |
| $\delta$[CCSD(T)] | +0.56 | +0.70 | [+0.70] | [+0.70] |
| $\Delta E_e$(corr) | −19.76 | −18.21 | [−18.34] | [−18.56] |
| $\Delta E_0 = \Delta E_e$[focal-point] + $\Delta$[ZPVE] = −18.56 + 5.35 = −13.21 | | | | |
| Reaction B: aziridine + $3C_2H_6$ → $CH_3NHCH_3$ + $2C_3H_8$ | | | | |
| $\Delta E_e$[RHF] | −25.68 | −24.17 | −24.12 | [−24.12] |
| $\delta$[MP2] | −1.68 | −2.08 | −2.43 | −2.82[c] |
| $\delta$[CCSD] | +0.14 | −0.08 | [−0.08] | [−0.08] |
| $\delta$[CCSD(T)] | −0.08 | −0.02 | [−0.02] | [−0.02] |
| $\Delta E_e$(corr) | −27.30 | −26.35 | [−26.65] | [−27.04] |
| $\Delta E_0 = \Delta E_e$[focal-point] + $\Delta$[ZPVE] = −27.04 + 3.03 = −24.01 | | | | |
| Reaction C: *trans*-diaziridine + $CH_4$ + $2NH_3$ → $2CH_3NH_2$ + $N_2H_4$ | | | | |
| $\Delta E_e$[RHF] | −13.49 | −12.43 | −12.53 | [−12.53] |
| $\delta$[MP2] | +6.72 | +6.43 | +6.08 | +5.65[c] |
| $\delta$[CCSD] | −2.06 | −2.64 | [−2.64] | [−2.64] |
| $\delta$[CCSD(T)] | +1.31 | +1.44 | [+1.44] | [+1.44] |
| $\delta$[BD(TQ)] | −0.01 | [−0.01] | [−0.01] | [−0.01] |
| $\Delta E_e$(corr) | −7.53 | [−7.21] | [−7.66] | [−8.09] |
| $\Delta E_0 = \Delta E_e$[focal-point] + $\Delta$[ZPVE] = −8.09 + 5.57 = −2.52 | | | | |
| Reaction D: *trans*-diaziridine + $N_2H_4$ + $2C_2H_6$ → $2CH_3NHNH_2$ + $C_3H_8$ | | | | |
| $\Delta E_e$[RHF] | −21.85 | −20.51 | −20.61 | [−20.61] |
| $\delta$[MP2] | +2.07 | +1.38 | +0.83 | +0.20[c] |
| $\delta$[CCSD] | −0.35 | −0.71 | [−0.71] | [−0.71] |
| $\delta$[CCSD(T)] | +0.57 | +0.64 | [+0.64] | [+0.64] |
| $\Delta E_e$(corr) | −19.56 | −19.20 | [−19.85] | [−20.48] |
| $\Delta E_0 = \Delta E_e$[focal-point] + $\Delta$[ZPVE] = −20.48 + 2.88 = −17.60 | | | | |

[a] All entries in kcal mol$^{-1}$. The symbol $\delta$ denotes the increment in the reaction energy ($\Delta E_e$) relative to the preceding level of theory. [b] Increments in brackets are assumed values. [c] Extrapolated to the infinite basis set limit (see text).

**TABLE 10: Zero-Point Vibrational Energies (ZPVE) and Thermochemical Data Used in the Determination of Heats of Formation[a]**

| | ZPVE[b] | $H°_{298.15} - H°_0$ | $\Delta H_f°_{298.15}$ |
|---|---|---|---|
| $H_2$(g) | | 2.024[c] | |
| $N_2$(g) | | 2.072[c] | |
| C(graphite) | | 0.251[c] | |
| $NH_3$(g) | 21.04 | 2.388[f] | −10.98 ± 0.08[d] |
| $N_2H_4$(g) | 32.59 | 2.655[f] | 22.79 ± 0.2[e] |
| $CH_4$(g) | 27.64 | 2.393[f] | −17.79 ± 0.10[d] |
| $C_2H_6$(g) | 46.01 | 2.784[f] | −20.03 ± 0.10[d] |
| $C_3H_8$(g) | 63.63 | 3.449[f] | −25.02 ± 0.12[d] |
| $CH_3NH_2$(g) | 39.32 | 2.730[f] | −5.50 ± 0.11[d] |
| $CH_3NHNH_2$(g) | 49.90 | 3.284[f] | 22.60 ± 0.15[d] |
| $CH_3NHCH_3$(g) | 56.78 | 3.358[f] | −4.45 ± 0.19[d] |
| aziridine(g) | 42.98 | 2.643[f] | |
| *trans*-diaziridine(g) | 35.94 | 2.589[f] | |

[a] All entries in kcal mol$^{-1}$. [b] Computed from 6-31G* MP2 harmonic vibrational frequencies scaled by 0.95. [c] Reference 70. [d] Reference 28. [e] Reference 71. [f] Computed employing 6-31G* MP2 frequencies scaled by 0.95 together with standard formulas from statistical mechanics.[66]

larger for reaction C than for D, and the cc-pVTZ CCSD → CCSD(T) increment in $\Delta E_e$ is sizable (+1.44 kcal mol$^{-1}$) for C. To investigate the effect of higher orders of correlation, the cc-pVDZ BD(TQ) reaction energy was therefore computed for reaction C. The cc-pVDZ CCSD(T) → BD(TQ) shift in $\Delta E_e$ was found to be only −0.01 kcal mol$^{-1}$, thus yielding support for the assumption that correlation beyond the CCSD(T) level can be neglected. We then advance a value of $\Delta H_f°_{298.15}$(*trans*-diaziridine) = 55.8 kcal mol$^{-1}$. To our knowledge, there are no other experimental or theoretical predictions for the heat of formation of diaziridine.

## Concluding Remarks

Optimum 6-31G* MP2 structures and harmonic vibrational frequencies have been computed for stationary points for nitrogen inversion on the ground-state potential energy surface for a series of aziridines and diaziridines, including the parent compounds aziridine and diaziridine and several methyl-substituted analogues. Accurate barriers to nitrogen inversion have been computed either by a high-level focal-point analysis or at the cc-pVQZ MP2 level of theory, which is demonstrated to predict barriers close to the focal-point value. Thermodynamic parameters $\Delta H^‡$, $\Delta S^‡$, and $\Delta G^‡$ and deuterium isotope effects for nitrogen inversion have been computed for several aziridines; the computed values generally agree well with the experimental results except for *trans*-2-methylaziridine, where the theoretical values for $\Delta H^‡$ and $\Delta S^‡$ seem incompatible with preliminary experimental results reported previously. Energetics have been computed at the cc-pVQZ MP2 level of theory for the conrotatory ring opening of aziridine, which forms an immonium ylide intermediate that may recyclize to form the nitrogen-inverted aziridine. Finally, accurate values have been computed for the heat of formation of aziridine and diaziridine using high-level focal-point analyses, and the values obtained are $\Delta H_f°_{298.15}$(aziridine) = 30.3 and $\Delta H_f°_{298.15}$(*trans*-diaziridine) = 55.8 kcal mol$^{-1}$. While the prediction for $\Delta H_f°_{298.15}$ (aziridine) confirms an earlier experimental value of 30.2 ± 0.2 kcal mol$^{-1}$, the result for diaziridine is a new contribution to the body of thermochemical data, as no prediction for $\Delta H_f°_{298.15}$(diaziridine) has been proposed previously.

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**Supporting Information Available:** Tables of harmonic vibrational frequencies for (*N*-D) isotopomers, total energies for nitrogen inversion in aziridine, and total energies and optimum geometries for species used in the determination of heats of formation (4 pages). Ordering information is given on any current masthead page.

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